Calcium Borosilicate Minerals from Devils Elbow, Nundle Area, New South Wales

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(Communicated by B. E. CHENHALL)

The relatively uncommon borosilicate minerals, datolite and axinite, occur in a vein paragenesis at Devils Elbow, near Nundle, northeastern New South Wales. Their paragenesis is a typical one, being within low-grade metamorphosed mafic rocks, limestone, cherty and volcaniclastic sediments of the Devonian Tamworth Group. Datolite is near stoichiometric in composition and is restricted to recrystallized limestone and cherty calcareous siltstone. Axinite is shown to be Fe-rich (ferroaxinite) and occurs in mafic rocks and volcaniclastic sandstone; host rock composition has influenced borosilicate mineral speciation. Vein formation has been attended by introduction of SiO_2, B_2O_3 and minor As, and, from fluid inclusion data, is estimated to have occurred at 230°C-280°C, at pressures approximating 1kb and from dilute NaCl fluids. Hydrothermal fluids are similar to those responsible for the formation of extensive Au-Sb-W-As-bearing veins in the Nundle district. Borosilicate veining cuts metamorphic assemblages in Tamworth Group rocks which are tentatively favoured to be the result of contact metamorphism by the subjacent Permian Duncans Creek Trondhjemite. Vein formation may be no older than late Permian and coeval with the Nundle Au-Sb-W-As vein mineralization event. Indeed, borosilicate veining is probably a continuum from the latter, with the boron possibly derived from marine sediments and mafic rocks previously enriched in the element by spilitization reactions.

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INTRODUCTION

The calcium borosilicate minerals have typical parageneses in skarns and calcsilicate rocks where boron metasomatism has occurred and as veins and replacements in low-temperature metamorphosed mafic igneous rocks (e.g. Deer *et al.*, 1962, 1986; Vallance, 1966). In these occurrences, they are associated with other calcsilicate minerals, tourmaline, calcite, quartz, fluorite, chlorite and albite.

In this paper, a vein paragenesis of datolite and axinite in limestone, mafic igneous rocks and clastic sediments is reported. During recent road widening operations, new exposures of vein minerals were afforded at Devils Elbow, 4km east-southeast of Nundle in northeastern New South Wales (Australian Map Grid Reference 9135-262161). Subsequent petrographic and electron microprobe examination confirmed the borosilicate phases. The location (Fig. 1) is within rocks assigned to the Silver Gully Formation of the Tamworth Group (Glenton, 1979; Ashley and Hartshorn, 1988) and is one of a number of axinite-bearing occurrences reported from the Nundle district. Benson (1913, 1915) was the first to report axinite, in association with quartz, epidote and calcite, in veins and vesicle fillings in mafic rocks of the Tamworth Group. Further occurrences were noted by Vallance (1960) and Glenton (1979) and the writer has found the mineral, with quartz and epidote, at a number of locations (e.g. G.R. 252258 and 264152) within mafic rocks of the Tamworth Group and Woolomin Group. Although the comparatively rare mineral datolite has been found in Tamworth Group equivalent rocks at Bundook, west of Taree (Vallance, 1960), its presence in the Nundle district does not appear to have been noted in the literature.
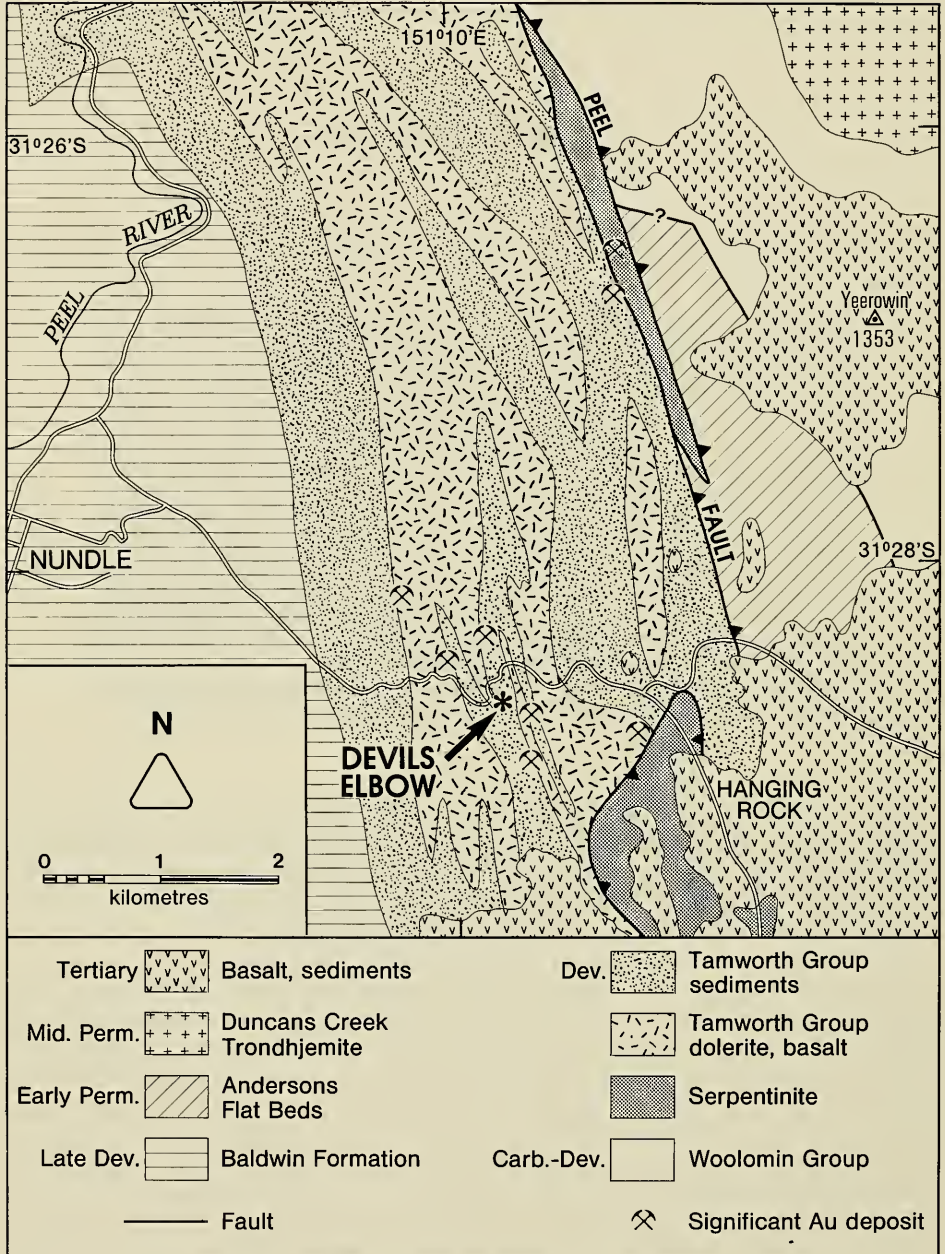
Fig. 1. Geology of the Nundle-Hanging Rock area, modified from Ashley and Hartshorn (1988), with location of Devils Elbow borosilicate mineral occurrence.

The Tamworth Group hosting the borosilicate minerals forms part of the Gamilaroi terrane of Flood and Aitchison (1988). It was deposited in the early to middle Devonian and consists of marine siltstone-argillite, volcaniclastic sandstone, spilitized mafic rocks (sills and flows), keratophyre, conglomerate and limestone (e.g. Benson, 1913, 1915; Vallance, 1960, 1969a, 1969b; Crook, 1961; Morris, 1988; Ashley and Hartshorn, 1988; Cawood and Flood, 1989). Recent interpretations favour the Tamworth Group to represent a dominantly volcaniclastic fore-arc sequence underlain by and intercalated with mafic igneous oceanic crustal rocks. The spilitized mafic rocks were favoured by Korsch (1977), Cross, (1983) and Morris(1988) to have developed as a result of rifting of the fore-arc basin, although Cawood and Flood (1989) suggest their generation in a magmatic arc. Tamworth Group rocks are bounded to the east by the Peel Fault, along which elements of the Great Serpentinite Belt (Weraerai terrane of Flood and Aitchison, 1988) have been emplaced. The Peel Fault separates the Tamworth Group from the Woolomin Group and Andersons Flat Beds (Djungati terrane of Flood and Aitchison, 1988), with the Woolomin Group having been intruded by the Permian Duncans Creek Trondhjemite (Fig. 1).

GEOLOGICAL SETTING AND PETROGRAPHY

At Devils Elbow, the Silver Gully Formation consists of low grade metamorphosed, well-bedded cherty calcareous siltstone grading to medium grained volcaniclastic sandstone, massive medium-grained dolerite and minor fine-grained basalt, and a distinctive recrystallized bioclastic limestone bed. There is commonly excellent preservation of primary sedimentary and igneous textures in the rocks and although the terms spilite and metabasite have been widely employed for the low grade mafic rocks of the Nundle district (e.g. Benson, 1915; Vallance, 1960, 1969b, 1974; Morris 1988; Cawood and Flood, 1989), use of pre-metamorphic rock terminology is preferred in this paper. The limestone bed was originally reported by Benson (1913) and informally termed Devils Elbow Limestone Member by Glenton (1979) and Pickett (1986). The sequence dips east-northeast at 70° and is probably overturned, based on district stratigraphic configuration. The dolerite may have intruded the limestone bed, as suggested by Benson (1913) and by a recently exposed prominent chilled margin on the sill-like mafic body. The limestone bed is approximately three metres thick, bounded to the west by dolerite and minor basalt, and to the east by siltstone and sandstone. Although recrystallized, the limestone contains a shelly and coralline fauna, and Pickett (1986) reported the presence of late early Devonian conodonts. Glenton (1979) suggested that the limestone has been redeposited and thus the fossil remains are not necessarily indicative of the age of the bed.

Vein assemblages occur in all lithologies but are most evident in limestone where they form steeply dipping, simple planar and anastomosing arrays up to 3cm wide which cut the stratigraphy at a high angle. Datolite-bearing veins occur in limestone (Fig. 2a) and siltstone whereas axinite-bearing assemblages appear to be restricted to the mafic igneous rocks (Fig. 2b) and volcaniclastic sandstone. The two borosilicate minerals have not been found together.

Datolite is found as pale brown and pale green to white aggregates in which squat barrel-shaped to prismatic grains attain a maximum grainsize of 3mm. Mostly, however, it forms a granular mosaic with a grainsize of <0.5mm. In the veins, the mineral is associated in apparent textural equilibrium with calcite and minor quartz, chlorite and prehnite. Datolite grains are unstrained, contain locally abundant fluid inclusions and have undergone slight intragranular retrogression to calcite. The latter is texturally distinct from the medium to coarse grained calcite coexisting in apparent
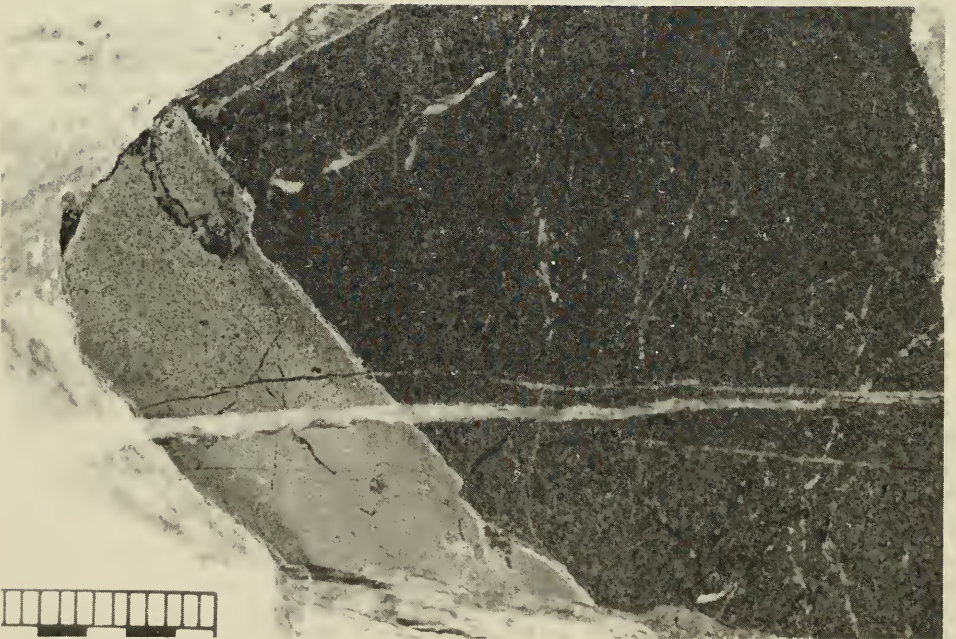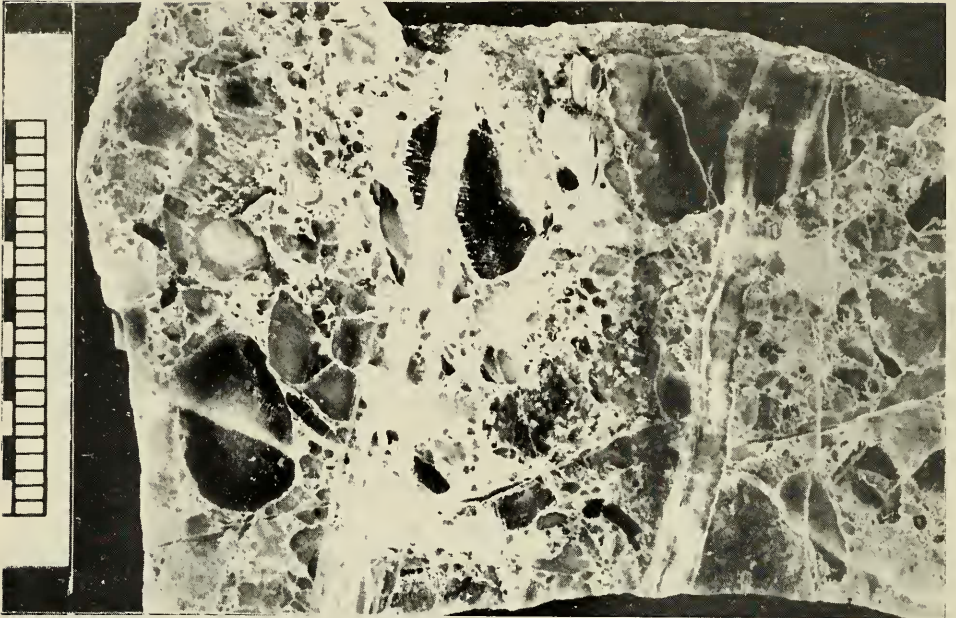
Fig. 2. **a.** Bioclastic limestone slab with fragments up to 4 cm across in a pale-coloured fine grained calcsilicate matrix and cut by planar datolite-quartz veins up to 7 mm wide. Scale is 5 cm long. Sample R63079, Devils Elbow. **b.** Slab showing contact between basalt (medium grey) and medium grained dolerite (dark grey) cut by planar axinite-quartz veins up to 8 mm wide. Scale is 2.5 cm long. Sample R63077, Devils Elbow.

equilibrium with datolite. Limestone in which datolite-bearing veins occur contains recrystallized calcite (commonly pseudomorphing bioclastic material) in a formerly calcareous muddy matrix now recrystallized to fine-grained aggregates of subhedral garnet and minor vesuvianite, diopside, clinozoisite, titanite (sphene), albite and apatite. Electron microprobe analyses of garnet show that it is grossular ($Gr_{93.4-95.2}Ad_{1.2-2.3}Al_{1.8-4.4}Sp_{0.1-0.2}Py_{0.6-0.8}$) and associated vesuvianite is relatively Mg-rich with a composition of $Ca_{9.1}Mg_{1.2}Fe_{0.8}Ti_{0.2}Al_{4.3}Si_{8.9}O_{34}(OH)_4$. The minor Fe in the rock is strongly partitioned into vesuvianite. Bedded siltstone hosting datolite-bearing veins contains volcaniclastic albitized plagioclase in a recrystallized cherty matrix studded with subradiating aggregates and prismatic grains of diopside and actinolite, plus minor titanite.

Axinite occurs as pale mauve prismatic grains up to 6mm long. Prisms are commonly aligned both parallel and normal to vein walls. Accompanying vein minerals are quartz, calcite, minor chlorite and traces of sphalerite and pyrrhotite. Although epidote accompanies axinite in many veins in the Nundle district, the association has not been observed at Devils Elbow. Axinite shows faint mauve and blue pleochroism and is incipiently replaced by calcite. Dolerite, basalt and volcaniclastic sandstone hosting axinite-bearing veins retain relict textures, with primary clinopyroxene and magnetite; other minerals, however, are metamorphic and include albite, actinolite, chlorite, epidote with traces of titanite, pyrite, chalcopyrite, pyrrhotite, pumpellyite, carbonate and quartz. Pumpellyite appears to be largely restricted to former calcic plagioclase cores.

CHEMISTRY OF BOROSILICATE MINERALS AND ENCLOSING ROCKS

Electron probe microanalysis was used to ascertain compositions of the borosilicate minerals but as boron was not able to be determined, the content of B_2O_3 (as well as H_2O) was calculated assuming stoichiometry. Datolite from the Devils Elbow veins proves to be close to $CaBSiO_4(OH)$ with analyses (Table 1) indicating insignificant substitution of other components. The results match other datolite analyses (e.g. Deer *et al.*, 1962) and the atomic Si:Ca ratio close to unity implies no substitution of the closely related bakerite $CaB_4BO_4(SiO_4)_3(OH)_3.H_2O$ molecule. Datolite coexists with essentially pure calcite in limestone and with minor ferrian prehnite and pycnochlorite (Table 1) in siltstone.

Axinites analysed from Devils Elbow are ferroaxinite in the classification of Sanero and Gottardi (1968), with Ca > 1.5 atoms per formula unit (pfu) and Fe > Mn (Table 1). Results from two samples show a considerable range in Mg, Fe and Mn contents with Mg being negatively correlated with Mn and Fe (Fig. 3). Consistent with other ferroaxinites, Ca is close to 2 atoms pfu, but the total Fe content of the mineral is particularly high, ranging toward the highest reported values (*cf.* Lumpkin and Ribbe, 1979; Deer *et al.*, 1986). Calcites coexisting with axinite include stoichiometric $CaCO_3$ in sample R63077 (University of New England, Department of Geology and Geophysics collection) and a manganoan variety ($Ca_{0.87}Mg_{0.02}Fe_{0.02}Mn_{0.09})CO_3$ in sample R63078. Associated chlorites are ripidolite (Table 1) which are richer in Fe and Mn than the pycnochlorites coexisting with datolite.

The fact that Ca borosilicate speciation and composition of associated minerals vary in different lithologies implies that bulk rock chemistry has influenced vein mineralogy, assuming that the vein fluids had relatively constant aB_2O_3. It is interpreted that datolite-bearing veins have formed in response to low Al, Fe, Mn and Mg contents of host limestone and siltstone, whereas the higher contents of these elements in mafic rocks and sandstone have resulted in the crystallization of axinite and relatively Fe-rich chlorite.

TABLE 1

Electron microprobe analyses of Devils Elbow borosilicate and associated vein minerals

	1	2	3	4	5	6	7	8
SiO_2	37.17	37.53	41.56	42.40	41.46	27.28	25.27	25.01
TiO_2			0.06	0.04	0.07			
Al_2O_3	0.03	0.02	18.15	18.65	21.71	19.18	19.49	19.11
B_2O_3*	21.76	21.76	6.20	6.22				
Cr_2O_3							0.04	
ΣFeO			8.91	7.73	4.16+	21.06	32.60	31.61
MnO			2.68	0.32		0.22	0.43	0.40
NiO						0.03		0.03
MgO			1.21	2.81		19.21	11.34	11.74
CaO	35.01	35.01	19.63	19.64	25.90	0.09	0.05	0.07
Na_2O		0.02	0.02					0.03
K_2O						0.01		
Total	93.97	94.34	98.42	97.81	93.30	87.08	89.22	88.00
	4.5(O)		31(O)		11(O)		28(O)	
B	1.003	1.000	2.023	2.005				
Si	0.994	1.000	7.859	7.922	2.964	5.657	5.460	5.463
Aliv	0.001		0.141	0.078	0.036	2.343	2.540	2.537
Alvi		0.001	3.904	4.031	1.797	2.344	2.420	2.382
Ti			0.009	0.006	0.004			
Cr							0.005	
ΣFe^{2+}			1.409	1.208	0.224+	3.653	5.890	5.775
Mn			0.430	0.051		0.039	0.078	0.073
Ni						0.005		0.005
Mg			0.341	0.783		5.937	3.651	3.821
Ca	1.003	0.999	3.977	3.932	1.984	0.019	0.011	0.016
Na		0.001	0.007					0.011
K						0.003		
Σ	3.003	3.001	20.100	20.016	7.009	20.000	20.055	20.083
mg			0.195	0.393		0.619	0.383	0.398

Analyst: P. M. Ashley. Cameca instrument, R.S.E.S., Australian National University, Canberra. Blank = below detection limit: Cr_2O_3 0.04%; FeO, MnO, NiO 0.03%; TiO_2, MgO, Na_2O 0.02%; K_2O 0.01%.
* B_2O_3 calculated. Total Fe as FeO, except in analysis 5 (+) where Fe is calculated as Fe_2O_3.

1. Datolite (average of 5 analyses) from datolite-ferrian prehnite-pycnochlorite-quartz vein in siltstone. Sample R63076.
2. Datolite (average of 6 analyses) from vein in limestone. Sample R63062.
3. Ferroaxinite (average of 7 analyses) from ferroaxinite-quartz-calcite-ripidolite vein in dolerite. Sample R63077.
4. Ferroaxinite (average of 4 analyses) from ferroaxinite-quartz-manganoan calcite-ripidolite vein in dolerite. Sample R63078.
5. Ferrian prehnite (average of 4 analyses) from analysis 1 assemblage. Sample R63076.
6. Pycnochlorite (average of 3 analyses) from analysis 1 assemblage. Sample R63076.
7. Ripidolite (average of 2 analyses) from analysis 4 assemblage. Sample R63078.
8. Ripidolite (average of 2 analyses) from analysis 3 assemblage. Sample R63077.
All samples in this paper are housed in the collection of the Department of Geology and Geophysics, University of New England.

Whole-rock chemical analyses have been carried out on two samples with conspicuous borosilicate veining and two on adjacent unveined material. Unveined limestone contains a relatively minor non-carbonate detrital component, expressed as SiO_2, Al_2O_3 and TiO_2 (Table 2). The B_2O_3 content (0.13%) is well above typical values for limestones (20 ppm B; Harder, 1974), perhaps implying at least local pervasive

introduction and permeation of B throughout the limestone. Datolite-veined limestone, in contrast, contains higher SiO_2, B_2O_3 and As (Table 2) suggesting addition of these components during vein formation. Small variations in other components are attributed to either primary heterogeneity in the limestone and/or dilution due to introduced material.
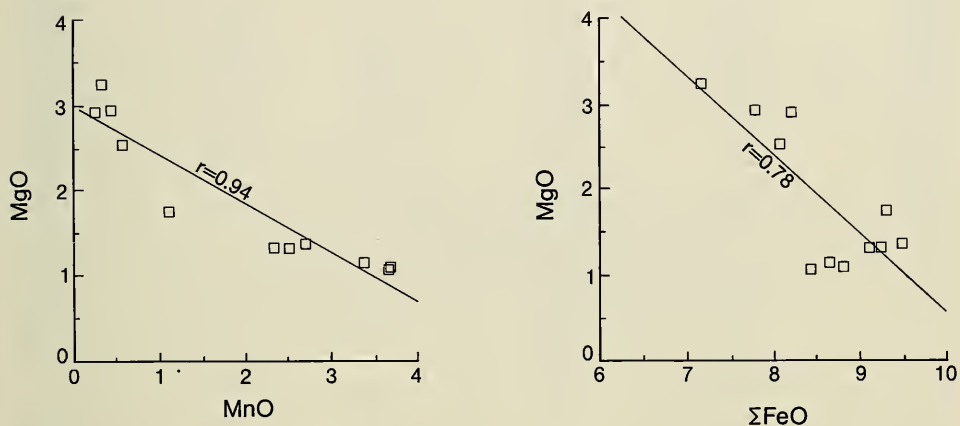

Fig.3. Weight percent MgO versus MnO and total FeO in ferroaxinites from Devils Elbow.

Unveined dolerite from Devils Elbow is compositionally similar to other mafic igneous rocks from the Tamworth Group in the Nundle district (e.g. Vallance, 1974; Cross, 1983; Morris, 1988; Ashley and Hartshorn, 1988). The composition (Table 2) is consistent with mid-ocean ridge basalt (MORB) although one relatively enriched in TiO_2, total FeO/MgO, P_2O_5, Zr, Y and V, and relatively low in MgO, Ni and Cr (*cf.* Sun *et al.*, 1979). In comparison to fresh MORB (e.g. Melson *et al.*, 1976; Sun *et al.*, 1979), the Nundle rocks are richer in H_2O, Na_2O, K_2O, Rb and Sr. These are mobile components which may have been introduced by hydrothermal interaction with seawater or perhaps represent enrichments due to element redistribution via spilitic degradation during burial metamorphism. The fact that the Nundle dolerites have constantly high Na_2O (compared to MORB values) (*cf.* Morris, 1988; Ashley and Hartshorn, 1988) and that complimentary volumes of Na-depleted dolerite are not recognized, implies that Na and other enriched components have been added from a marine reservoir. Typical MORB basalt contains 2-8 ppm B (Humphris and Thompson, 1978; Seyfried *et al.*, 1984), although recent analyses by Spivack and Edmond (1987) of genuinely fresh MORB glasses yielded values of 0.2-0.4 ppm B. In any case, the value of 0.05% B_2O_3 in the unveined dolerite sample R63065 (Table 2) implies significant B addition. Such addition is logically from an ultimately marine source, as seawater contains on average 4.35 ppm B (e.g. Seyfried *et al.*, 1984) and that MORB-type basalts have been shown to be sinks for marine B during low and intermediate temperature hydrous alteration (Spivack and Edmond, 1987).

TABLE 2

Whole rock analyses of borosilicate-veined samples and adjacent rocks, Devils Elbow.

Sample	R63062	R63063	R63064	R63065	Av. TGM
SiO_2	15.03	6.07	52.92	50.20	49.41
TiO_2	0.14	0.11	2.02	2.19	2.22
Al_2O_3	2.01	1.55	14.23	13.41	13.85
Fe_2O_3	0.81	0.57	2.23	4.03	13.84*
FeO	0.34	0.31	6.24	8.83	
MnO	0.09	0.10	0.26	0.18	0.21
MgO	1.01	0.98	4.67	5.14	4.51
CaO	46.69	52.10	8.27	7.21	7.29
Na_2O	0.01	0.02	5.20	4.87	4.79
K_2O	0.07	0.04	0.51	0.74	0.39
P_2O_5	0.04	0.03	0.25	0.25	0.29
B_2O_3	5.26	0.13	0.78	0.05	
S	0.02	0.02	0.02	0.04	0.13
L.O.I.	28.91	37.97	2.35	2.43	2.87
less O = S	0.01	0.01	0.01	0.02	0.06
Total	100.42	99.99	99.94	99.55	99.74

			Trace elements ppm		
Li	<7	<7	7	11	
Ba	28	<5	93	158	74
Rb	2	1	6	10	5
Sr	147	184	211	347	235
U	2	3	<1	1	
Th	2	3	<1	<1	
Y	9	6	47	44	46
Zr	12	10	142	120	134
Nb	1	1	3	2	3
Ce	4	11	21	21	21
Nd	9	13	17	17	
La	5	2	5	5	8
Ga	5	3	16	15	20
Sc	<1	<1	43	47	38
V	24	12	405	546	407
Ni	6	6	26	24	22
Cr	42	24	48	32	21
Cu	16	16	6	13	47
Pb	<1	3	2	<1	<1
Zn	13	13	49	49	102
As	34	<1	32	5	4

Analysts: J. Bedford, J. Cook. Analyses by XRF except for FeO (titrimetry), L.O.I. (loss-on-ignition) (gravimetry), B_2O_3 and Li (ICP).
* Total Fe as Fe_2O_3. Blank = not determined.

R63062: Datolite-veined recrystallized limestone (containing minor grossular, vesuvianite and diopside).
R63063: Unveined recrystallized limestone with minor grossular, vesuvianite and diopside.
R63064: Axinite-veined dolerite.
R63065: Massive unveined dolerite.
Av TGM: Average of 30 Nundle area Tamworth Group dolerites and basalts from Ashley and Hartshorn (1988) (includes data from Morris, 1988).

Samples prefixed "R" from Australian Map Grid Reference 9135-262161.

In comparison to unveined material, dolerite with axinite-bearing veins is richer in SiO_2, B_2O_3 and As (Table 2) showing that the chemical changes are identical to those

operative in the formation of the datolite-veined limestone. Other minor chemical disparities may again be possibly attributed to primary heterogeneity and/or dilution effects.

Fluid Inclusions in Datolite-bearing Veins

Fluid inclusions are locally abundant in the vein minerals calcite, datolite, axinite and quartz. However, only in the datolite-bearing veins were they large enough (typically in the range $3\text{-}20\mu m$ across) to yield microthermometric data. The most suitable inclusions were found in a limestone-hosted, medium to coarse grained calcite-datolite vein in which the minerals appeared to be in textural equilibrium. Inclusions are primary and pseudosecondary types using the criteria of Roedder (1984), and show simple two-phase character with a constant liquid-to-vapour ratio of about 9:1. Those in calcite commonly display negative rhombohedral crystal shape whereas in datolite, inclusions tend to be more ovoid, prismatic or irregular. Microthermometric determinations were carried out on a SGE heating stage which had been calibrated with chemicals of accurately known melting point (methyl benzoate, distilled H_2O, benzoic acid, $NaNO_3$, $K_2Cr_2O_7$, $PbCl_2$).

Heating runs on fluid inclusions in calcite yielded a range in homogenization temperature (T_h) of $140°\text{-}217°C$, with a mean T_h of $183°C$; inclusions in datolite have a T_h range of $145°\text{-}209°C$ (mean $T_h = 171°C$) (Fig. 4). The difference in mean T_h between datolite- and calcite-hosted inclusions is not considered significant due to the small number of measurements obtained on datolite. All inclusions homogenized to the liquid phase and repeat determinations yielded a precision of $\pm 5°C$.

Freezing runs to determine the melting temperature of ice (T_m) were difficult due to small size of inclusions and the double refraction of calcite. However, several inclusions in datolite yielded a value of T_m of $-1.4 \pm 0.5°C$. Using the equations of Potter *et al.* (1978), this value converts to 2.3 ± 0.8 equivalent weight (ewt) % NaCl. The calculated fluid salinity is probably a maximum value as it assumes no contribution to freezing point depression by dissolved CO_2 which has been shown to give erroneously high calculated equivalent NaCl values (Hedenquist and Henley, 1985). As vein calcite accompanies the borosilicates, it is implicit that CO_2 was at least a minor fluid component and thus NaCl values are likely to be < 2.3 ewt %.

There is no evidence for boiling or effervescence in fluid inclusions in the borosilicate-bearing veins (i.e. trapping of coexisting liquid- and vapour-rich inclusions). Thus the pressure on the fluid at the time of entrapment was greater than the vapour pressure and hence a pressure correction must be applied. From the boiling curves of Haas (1971), it is estimated that at least 100 m of cover (at hydrostatic pressure) would be needed to prevent fluids of 2.3 ewt % NaCl from boiling at 180°C (the approximate average of all vein fluid inclusion T_h values; Fig. 4). This estimate is clearly a minimum as current topographic relief between Devils Elbow and the Tertiary basalt-capped plateau to the east (Fig. 1) is 200-250 m. A more realistic depth of formation for the veins would be approximately 2-4 km, based on analogies with quartz veins hosting Au-Sb-W-As mineralization in the Nundle area and the southern part of the New England Orogen generally (e.g. Comsti and Taylor, 1984; Nano, 1987; Ashley and Hartshorn, 1988) and the fact that the vein-controlling structures are brittle phenomena. On this assumption, lithostatic pressures would be in the range 0.6-1.2 kb and would require a pressure correction of $+50\text{-}100°C$, utilizing the curves of Potter (1977). This would imply that the borosilicate-bearing veins formed at an average temperature of between 230° and 280°C.

The estimated conditions for vein formation and the nature of the vein fluids are

somewhat similar to those deduced for the vein Au-Sb-W-As occurrences in the Nundle district. T_h data from over 370 fluid inclusions in these veins have an uncorrected range of 139°365°C, with a bimodal distribution of T_h at 190°C and 250°C. Ashley and Hartshorn (1988) also showed that the fluids were CO_2-bearing and averaged 4 ewt % NaCl. Applying the above pressure correction to the Au vein data, the bimodal peaks fall at approximately 260°C and 320°C. It would therefore appear that the borosilicate veins formed under conditions analogous to the lower part of the T_h spectrum for the Au veins.
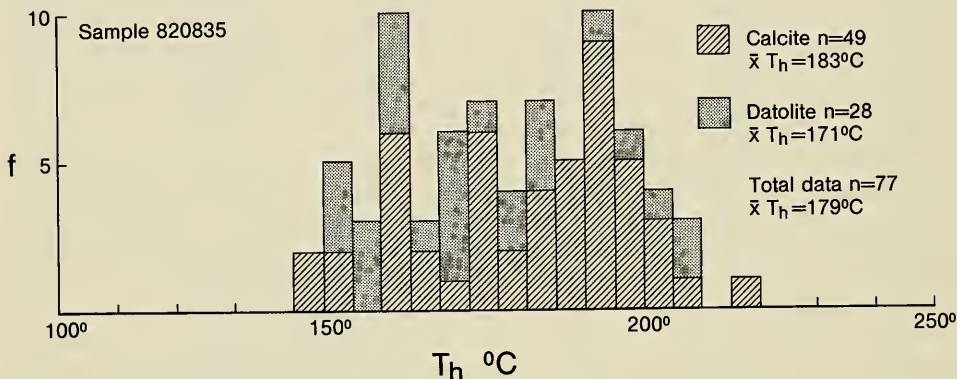
Fig. 4. Fluid inclusion homogenization temperatures (T_h) from vein calcite and datolite, sample R63080, Devils Elbow.

DISCUSSION

Metamorphism and Timing of Vein Formation. Rocks hosting the borosilicate-bearing veins at Devils Elbow have the following (non-vein) critical metamorphic parageneses:

1) Limestone: grossular + diopside + vesuvianite + calcite + clinozoisite;
2) Siltstone: actinolite + diopside; and
3) Dolerite: actinolite + chlorite + epidote + titanite ± pumpellyite.

If it is assumed that pressure operative in the metamorphism (which was static in character) was relatively low, e.g., approximating 2 kb, then the assemblages indicate temperatures of at least 400°425°C with a low mole fraction (X) of CO_2 (X_{CO2} probably < 0.02). These parameters are suggested by the presence of vesuvianite (in the absence of quartz) (e.g., Hochella *et al.*, 1982), presence of grossular and absence of prehnite (in non-vein assemblages) (e.g., Liou, 1971; Winkler, 1979; Liou *et al.*, 1985). Although diopside may form below 350°C, its occurrence further confirms low values of X_{CO2} (e.g. Labotka *et al.*, 1988). Since the mafic rocks contain typical actinolite + chlorite + titanite assemblages, maximum temperatures at 2 kb (and at oxygen fugacities below the hematite-magnetite buffer) are not likely to have exceeded 450°475°C, according to the experimental work of Moody *et al.* (1983). The occurrence of pumpellyite in the dolerite raises problems as Schiffman and Liou (1980) have shown that at low pressures (2-3 kb), MgAl pumpellyite is stable only to temperatures of 330°350°C. It is possible that the mineral is metastable, having been insulated from prograde breakdown reactions by its typical occurrence in albitized plagioclase cores.

Mafic and volcaniclastic rocks in the Gamilaroi terrane elsewhere in the Nundle district characteristically contain albite + chlorite + titanite $\pm$ prehnite $\pm$ pumpellyite $\pm$ actinolite $\pm$ epidote $\pm$ carbonate $\pm$ relict clinopyroxene $\pm$ magnetite (e.g. Benson, 1915; Vallance, 1960; Chappell, 1968; Cross, 1974; Morris, 1988; Ashley and Hartshorn, 1988). Such assemblages probably straddle the prehnite-actinolite and prehnite-pumpellyite facies, which at pressures of < 3 kb are restricted to temperatures below 350°C (e.g. Liou *et al.*, 1985). The presence of apparently higher-grade rocks at Devils Elbow are interpreted as the result of later thermal metamorphism by the Permian Duncans Creek Trondhjemite which crops out 6 km to the northeast (Fig. 1) but probably underlies a considerable region to the west and south of the intrusion. This concept is consistent with the occurrence of contact metamorphosed dolerite and sediments elsewhere east of Nundle (Morris, 1988) and with the fact that much of the serpentinite along the Peel Fault in the area is antigoritic (Ashley and Hartshorn, 1988).

The borosilicate-bearing veins cut the metamorphic assemblages and thus if the latter are related to the intrusion of the Duncans Creek Trondhjemite, then the former must be no older than middle to late Permian (e.g. Cross, 1983; Hensel *et al.*, 1985). Timing of the borosilicate veins could therefore be the same as that deduced by Ashley and Hartshorn (1988) for the formation of the vein Au-Sb-W-As mineralization in the Nundle goldfield, that is, probably no older than late Permian. It is also possible that the borosilicate veins are simply another manifestation of the Nundle goldfield veining, examples of which occur within 300 m of Devils Elbow. Borosilicate veining may be temporally related to the same vein-forming thermal event and to similar brittle-style structural control. It is probably no coincidence that the borosilicate-veined samples are anomalous in As (Table 2) and that rare tourmaline occurs in alteration selvedges about Au-bearing veins in the Nundle goldfield (Ashley and Hartshorn, 1988).

Conditions of Vein Formation and Component Sources. Field and petrographic evidence dictate that the borosilicate-bearing veins post-date the host rock metamorphic assemblage which may have developed at 400°-450°C and pressures < 3 kb. From fluid inclusion and mineralogical data, the veins formed at 230°-280°C and possibly at pressures of 0.6-1.2 kb. Hydrothermal fluids were dilute (< 2.3 ewt % NaCl), possibly CO_2-bearing and transported SiO_2, B and As in solution. The source of these components is speculative with possible alternatives including the enclosing marine sedimentary and basaltic package, granitic intrusives or from deeper crustal metamorphic devolatilization reactions. An intrusive-related magmatic source is considered unlikely for B as the nearby Nundle Suite intrusives (e.g. Duncans Creek Tronhjemite) are not known to contain late- or post-magmatic tourmaline and have primitive I-type (metaluminous) characteristics (e.g. Hensel *et al.*, 1985). These properties are quite unlike tourmaline-bearing granites which are typically felsic peraluminous in nature (e.g. Pollard *et al.*, 1987). A source of B from marine sediments (e.g. shales average 120 p.p.m. B; Harder, 1974) or from B previously fixed in basaltic rocks by interaction with seawater (e.g. Spivack and Edmond, 1987) is considered more plausible for the Devils Elbow borosilicates and for axinite occurrences elsewhere in the Nundle district. Remobilization of B from this source may have attended the shallow crustal hydrothermal fluid circulation accompanying the formation of the Nundle goldfield Au-Sb-W-As veins. Confirmation of these speculations may have to rely on future stable isotope determinations, including $\partial^{11}B$ values for the vein borosilicate minerals.

<div align="center">SUMMARY AND CONCLUSIONS</div>

The calcium borosilicate mineral axinite has been known for many years in mafic

rocks of the Devonian Tamworth Group in the Nundle district (e.g. Benson, 1913). However, new exposures at Devils Elbow, 4 km east-southeast of Nundle, have revealed simple and anastomosing veins containing axinite and the comparatively rare borosilicate, datolite. The veins, up to 3 cm wide, occupy brittle structures in steeply dipping recrystallized bioclastic limestone (informally termed Devils Elbow Limestone Member), massive dolerite and basalt, and bedded cherty calcareous siltstone grading into volcaniclastic sandstone. Datolite-bearing veins, containing associated calcite, quartz, chlorite and prehnite, are restricted to the limestone and cherty calcareous siltstone whereas axinite-bearing veins, with associated quartz, calcite and chlorite, occur within the mafic rocks and volcaniclastic sandstone. It is probable that host rock composition has influenced the speciation of the borosilicates, i.e. datolite being found in rocks with low Fe, Mn and Al contents and axinite in rocks with significantly greater concentrations of these elements.

Datolite is pale brown, pale green or white and analyses indicate it is close to stoichiometric $CaBSiO_4(OH)$. Axinite forms pale mauve prisms compositionally falling into the ferroaxinite field of Sanero and Gottardi (1968). There is a considerable range of Mg, Fe and Mn contents with Mg being negatively correlated with Fe and Mn. Whole rock chemical analyses of veined and unveined samples of limestone and dolerite indicate that SiO_2, B and minor As were introduced during the vein-forming event. Background B concentrations in the host limestone and dolerite are considerably enriched above values for average limestone and MORB-type basaltic rocks (cf. Harder, 1974; Spivack and Edmond, 1987) and could imply prior introduction from a seawater source.

Vein minerals contain simple 2-phase fluid inclusions, although only those in calcite and datolite were large enough to obtain microthermometric data. Homogenization temperatures range from 140°-217°C with a mean of 179°C and although only a few inclusions were suitable for freezing point determination, an ice melting temperature of -1.4° ± 0.5°C was obtained, indicating a maximum fluid salinity of 2.3 ewt % NaCl. CO_2 is likely to have been at least a minor component of the fluid which was not boiling or effervescing. Based on an assumed depth of formation of 2-4 km for the borosilicate veins (similar to deduced formation depths of Au-Sb-W-As-bearing veins in the Nundle district and elsewhere in the southern part of the New England Orogen), a pressure correction of +50°-100°C on the T_h values is required, yielding average vein formation temperatures in the range 230°-280°C.

Estimated vein formation conditions are at lower temperatures than those enjoyed by the enclosing rocks which show anomalously high metamorphic grade in comparison to Tamworth Group rocks elsewhere in the Nundle district. Metamorphic temperatures in the Devils Elbow-Hanging Rock area may have attained 400°-450°C and are attributed to contact effects of the nearby (?underlying) Permian Duncans Creek Trondhjemite. As borosilicate-bearing veins cut the metamorphic assemblages, the vein formation may be no older than late Permian and therefore probably coeval with the Nundle goldfield vein Au-Sb-W-As mineralization.

It is concluded that borosilicate-bearing veins at Devils Elbow, and elsewhere in the Nundle district, are another manifestation of the extensive Au-bearing vein systems. Borosilicate veins formed at slightly lower temperature and from more dilute hydrothermal fluids, but are otherwise not dissimilar (cf. Ashley and Hartshorn, 1988). Tourmaline occurs locally in association with the former, and As is anomalous in the latter; these chemical phenomena are viewed as common links. The source of B for the veins is unlikely to have been from granitic intrusives in the region, but could have been remobilized from marine sediments and mafic rocks which had undergone prior B fixation from seawater. The vein-forming event in the Nundle district, including both

the Au-Sb-W-As- and borosilicate-bearing veins, could be temporally related to the intrusion of the nearby Nundle Suite granitoids (e.g. Duncans Creek Trondhjemite and Mt Ephraim Granodiorite), but evidence from the mineralized veins suggests that the veining and hydrothermal activity is later (Ashley and Hartshorn, 1988). An alternative view is that the event is linked temporally to the intrusion of the late Permian Moonbi Suite plutons in the southern New England Orogen, not necessarily to the intrusives directly, but to the causative deep crustal thermal regime.

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